40

ON THE INTENSITY-DISTRIBUTION IN THE WING OF THE RAYLEIGH LINE DUE TO LIQUID OXYGEN*

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Plate XI

ABSTRACT—The intensity-distribution in the wing accompanying Rayleigh radiation from liquid oxygen has been studied quantitatively by the method of photographic spectrophotometry, using a suitable spectrograph and Hg 4047Å line as exciting radiation. It has been shown that the intensity distribution in the wing shows a clear maximum at about 40 cm^{-1} from the centre of the exciting line and the intensity, instead of increasing continuously as the centre of the line is approached, falls off and becomes zero at a distance of 9 cm^{-1} from the centre of exciting line. The probable causes of the discrepancy between this result and that reported by Crawford *et al* (1952) have been discussed.

INTRODUCTION

It is well known that the wing which accompanies the Rayleigh line due to molecules in the gaseous state generally consists of discrete lines, while in the case of organic liquids the wing shows a continuous intensity-distribution. The question whether in the case of heavy diatomic molecules in the liquid state, such as O_2, the rotational lines are resolved from each other as in the gaseous state was first investigated by Saha (1940). He observed a continuous wing in the neighbourhood of the Rayleigh line due to liquid oxygen and the intensity-distribution showed a maximum at a distance of 50 cm^{-1} from the Rayleigh line. These results, when compared with those reported by Trumpy (1933) for gaseous oxygen at a pressure of 60 atmosphers, show that the change of state has a marked influence on the width of rotational lines. Trumpy (1933) observed diserete rotational lines with the line of maximum intensity at a distance of 60 cm^{-1} from the Rayliegh line and the lines were slightly broader than those observed in the case of the gas at ordinary pressures. Recently, Crawford *et al* (1952) have investigated the distribution of intensity in the wing due to O_2, N_2 and CH_4 in the liquid state. In the case of liquid oxygen they also have observed a continuous wing, but they have failed to notice any maximum in the intensity-distribution. They attributed this discrepancy to the fact

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that Saha did not take into account the blackening produced by the Rayleigh line in its neighbourhood owing to over-exposure. On examining the microphotometric records of the incident and scattered lines reproduced by Saha (1940), however, it was observed by the present author that there was an inflexion in the curve in the record of the scattered line and this hump was absent in the record due to the incident line. It was, therefore, thought worthwhile to reinvestigate the Raman spectrum of liquid oxygen, using an arrangement in which stray light could be reduced as much as possible so as to avoid over-exposure of the Rayleigh line and a spectrograph which would give a suitable dispersion and an image of the slit free from coma. Fortunately, such a spectrograph was available in the laboratory and with this the Raman spectrum of a column of liquid oxygen, about 15 cm long, has been photographed. The results of analysis of the spectrum are discussed in the present paper.

EXPERIMENTAL

The experimental arrangement used in the present investigation was a simple one as shown in figure 1. *D* is a Dewar flask made of Pyrex glass, the walls at the bottom of which are blown flat so as to make the central areas plane and almost parallel to each other. The tube *T* containing liquid air is held in a vertical position and aligned centrally with the help

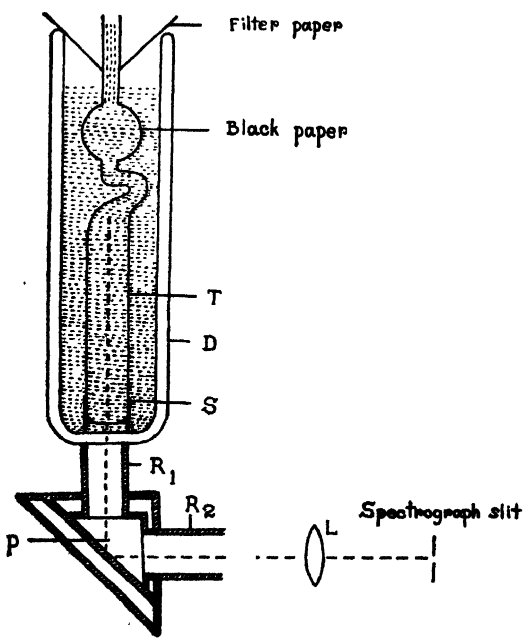


FIG. 1

of a stand and a collar *S* inside the Dewar flask *D* containing liquid air. The outer surface of the Dewar flask *D*, excepting the window

Fig. 2

Fig. 3

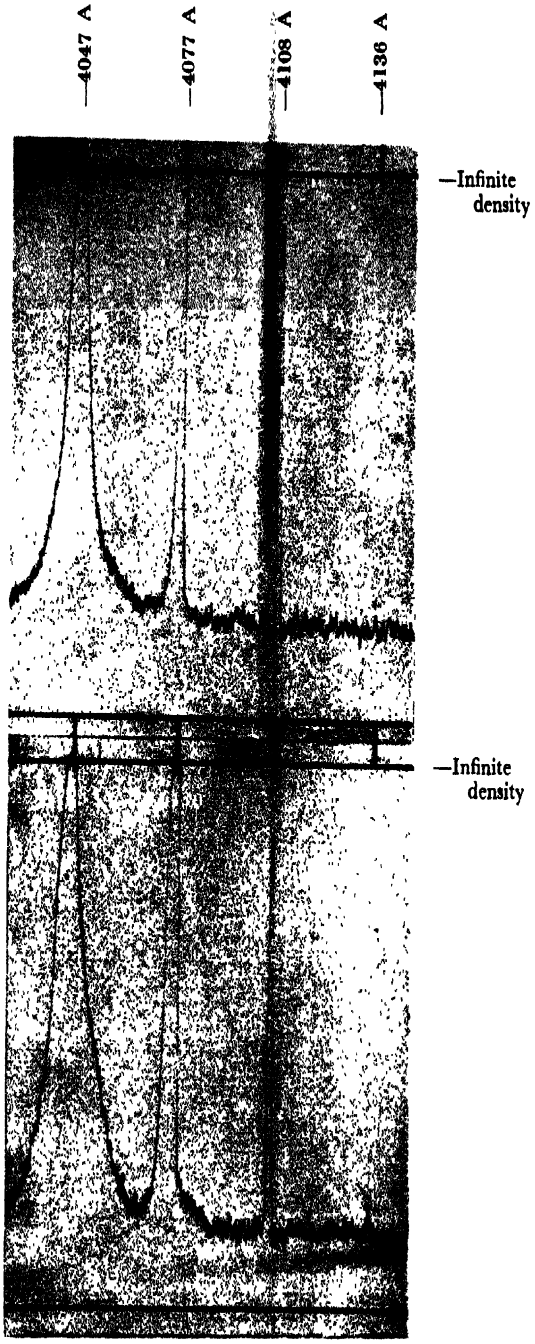


Fig. 2—Microphotometric record of Hg 4047 A group (incident)

Fig. 3 —Microphotometric record of Hg 4047 A group scattered by liquid O_2.

at the bottom and two fairly long parallel apertures on either side used for illuminatinting the liquid is painted dull black. The tube T is provided with a flat window at the lower end which reaches almost the bottom of the Dewar flask, and the other end is blown into the shape of a horn, the outer surface of which is covered with black paper. The collar S and the black paper tube surrounding the lower end of the tube T serve the purpose of preventing direct light from the mercury arcs and the light scattered by the outer liquid oxygen envelope from reaching the window of the tube.

The Dewar flask with the Wood's tube T was clamped with suitable clamps and placed vertically on the box B containing a totally reflecting prism P. Two long tubes R_1 and R_2 were attached at right angles to the prism box in order to reduce stray light as far as possible. The whole arrangement was then aligned accurately along the optical axis of the spectrograph and the scattered light was focussed on the slit of the spectrograph with the lens L. The Dewar flask D and the tube T were filled simultaneously with liquid oxygen filtered through filter papers, so that no ice was deposited on the window of the tube T. Though bubbles were formed in the liquid oxygen contained in the Dewar flask, the liquid oxygen inside tube T was free from such bubbles. Liquid oxygen was replenished from time to time in the Dewar flask as well as in the tube so that the level of the liquid oxygen in the tube was always below that of the liquid oxygen in the Dewar flask.

The liquid oxygen in the tube T was illuminated with the light from two vertical mercury arcs, through the transparent windows on the outer wall of the Dewar flask. The scattered light from the back end of the Wood's tube T was focussed with the condensing lens L, on the slit of a Fuess spectrograph. This spectrograph has a dispersion of 11 Å/mm in the region 4047Å. The aperature of the condensing lens L was adjusted so that the scattered beam entering into the spectrograph filled up about $\frac{3}{4}$ths of the aperature of the colliminating lens. The image of the slit produced by the spectrograph with this arrangement was free from coma on the Stokes side. The width of the slit was .04 mm.

Ilford Special Rapid plates were used to photograph the spectra. These plates were suitably backed to prevent the formation of haloes. An exposure of three and a half hours was sufficient to bring out the wing and the vibrational Raman line of liquid oxygen with moderate intensity. By trial, the spectrum of light from the mercury arc was recorded on a plate from the same packet, using different exposures so that the fourth mercury line of 4047 Å group was of the same density as in the spectrogram due to scattered light. The plates were developed under identical conditions.

For the purpose of calculating intensities from the densities in the neighbourhood of the Hg-line 4047Å in the spectra due to scattered and incident light, intensity marks were taken on a plate from the same packet, using tungsten filament lamp as the source of continuous radiation and varying the width of the slit of the spectrograph.

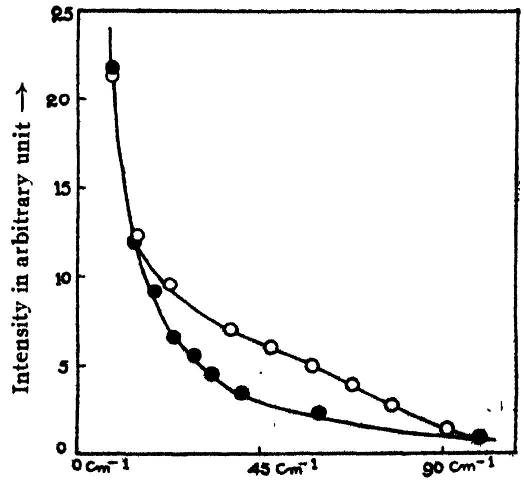
Microphotometric traces of the spectrograms and intensity marks were recorded with a Moll recording Microphotometer taking all sorts of necessary precautions. From the traces of the intensity marks a density *vs.* log intensity curve was drawn for the wavelength 4050 Å.

Care was taken to take the microphotometric records through corresponding points of the 4047 Å line in the scattered and incident spectra so that the distance between the centres of the lines 4108 Å and 4047 Å was exactly the same in both the records.

The values of intensity on the Stokes side of the scattered Hg-line 4047 Å were calculated for different distances from the centre of the 4047 Å line. The centre was located by measuring the distance from the 4108Å line. On the spectrogram due to incident light the intensities at the corresponding points on the Stokes side of the incident line 4047 Å were also calculated in the same way and these were deducted from the intensity values obtained for the spectrum of the scattered light. Each of these values were corrected for back-ground intensity and the final values for intensity were plotted as ordinates against wavenumber separation from the centre of the line 4047 Å as abscissa.

RESULTS AND DISCUSSION

The microphotometric records are reproduced in figures 2 and 3 (Plate XI). The relative intensities at different distances from the centre of the 4047 Å line in the spectra due to incident and scattered light are plotted in figure 4. It will be seen from figures 2 and 3 that the fourth line of the

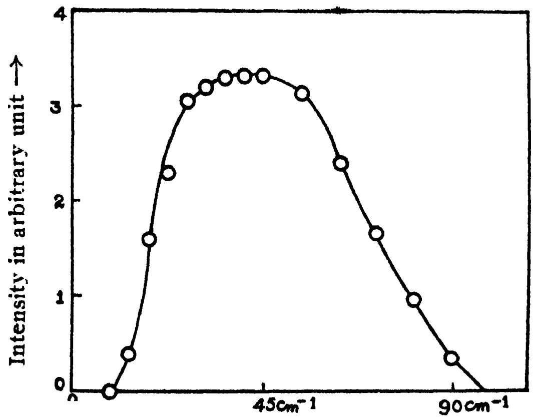


Distance from the centre of Hg 4047Å line in wavenumber →

FIG. 4.

Black circles give intensity of incident radiation and white circles give intensity of scattered radiation.

4047 Å group of mercury lines is of the same intensity in both the spectra due to the incident and scattered light respectively and figure 4 shows that upto a distance of about 9 cm^{-1} from the centre of the 4047 Å line the intensity distribution in the spectrum of the scattered light is exactly the same as that in the spectrum due to the incident light. As the distance increases further the intensity in the spectrum due to scattered light is larger than that in the incident spectrum and the difference between the two values first increases and then gradually falls off to zero as shown in figure 5. This difference is due to the rotational Raman spectrum and it shows a maximum at a distance 40 cm from the centre of Rayleigh line. It may be mentioned that the 1550 cm^{-1} line of O_2 was recorded with almost three times the intensity of Hg line 4136 Å.



Distance from the centre of Hg 4047Å line in wavenumbers →

Fig. 5

Difference of intensity between the scattered and incident radiation

The results obtained in the present investigation support the conclusion arrived at by Saha (1940) that in the case of liquid oxygen the intensity distribution in the wing accompanying the Rayleigh line has a maximum not at the centre of the Rayleigh line but at a certain distance from it. This distance was given by him as 50 cm^{-1}, but in the present investigation the quantitative curve showing the intensity distribution gives the position of the maximum at about 40 cm^{-1} from the centre of the Rayleigh line. The conclusion drawn by Crawford *et al* (1952) that the maximum lies at the centre of the Rayleigh line is not correct. It is difficult to account for the discrepancy between the results obtained by them and those of the present investigation. It has to be pointed out in this connection, however, that if any coma be present on the Stokes side of the line 4047 Å, its extent will depend on the method of focussing the light on the slit of the spectrograph and the extent of the coma in the line due to the incident light may not be identical with that in the line due to scattered light and in that case it is difficult to get correct information regarding the distribution of intensity in the wing. It is therefore essentially necessary to use a spectrograph which, besides having sufficient dispersion, should produce no coma even when the wing is over-exposed. It is almost impossible to get such a spectrograph, but fortunately, out of half a dozen Fuess spectrographs of this laboratory one was found to produce absolutely no coma on the Stokes side of the 4047 Å line even when the Hg 4136 Å line was recorded with moderate intensity, and the dispersion was quite sufficient. Secondly, in such an investigation the incident line has to be chosen carefully so that there is no band in the neighbourhood of the line at least on one side. Hg 2537 Å line is not suitable, because it is always accompanied by a band and a wing on the Stokes side. The 4047 Å line appears to be most suitable for the purpose of the present investigation as can be seen from microphotometric records reproduced in figure 2. Probably, Crawford *et ai* used the line 2537 Å as the exciting line and in that case it would be difficult to get the intensities due to incident line correctly.

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